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TITANIUM ALLOYS HAVING IMPROVED CASTABILITY

Cross-reference to Related Application

The present application is a continuation-in-part application of U.S. Patent Application Serial Number 10/179,310, filed June 26, 2002, which is a continuation-in-part application of U.S. Patent Application Serial Number 09/548,266, filed April 12, 2000, now US Patent Number 6,572,815B1. The above-listed US Patent Number 6,572,815B1 and Application Serial Number 10/179,310 are commonly assigned with the present invention and the entire contents of which are incorporated herein by reference.

Field of the Invention:

The present invention relates to a titanium alloy, and more particularly to a titanium alloy casting. The present invention provides a method to improve the castability of a titanium alloy, so that it is more suitable for use in making a dental casting and a medical implant.

Background of the Invention

Due to its lightweight, high strength-to-weight ratio, low elastic modulus, superior chemical corrosion resistance, and excellent mechanical properties at high temperature up to 550°C, titanium and its alloys have been widely used on aerospace, chemical, sports, and marine industries. Their superior biocompatibility also makes them ideal as the primary materials used in dental and osteological restorations or implants, such as artificial bone pins, bone plates, shoulders, elbows, hips, knees and other joints, and dental orthopraxy lines.

A number of methods for fabricating titanium and its alloys with a desired shape have been developed. Among these, precision casting is the most difficult. Precision casting has the advantage that the cast produced has a near net shape, which greatly decreases the titanium fabrication cost. Also, precision casting is particularly suitable for producing objects with a small volume, high size accuracy, and complicated shape, for example in dental and

osteological fields. Moreover, titanium and its alloys could even be utilized in many other everyday products, if the difficulty in precision casting could be solved.

There are many factors that affect the process of the precision casting and the properties of castings. According to the research results issued by Luk et al., in Dent. Mater., 8, 89-99, 1992, the factors include alloy composition, alloy density, alloy surface tension, casting temperature, investment material type, mold temperature, casting machine type, casting surface area/volume ratio, and pouring angle. The castability test is the most frequently used method for assessing various titanium precision casting processes. Castability is the ability of a molten alloy to completely fill a mold space. Castability is a combination factor, and there is no international standard for assessing it today. Since castability is affected by many factors, researchers have designed various test methods in accordance with various cast patterns for assessing the castability. The cast patterns include spiral wax molds, fibrous nylon lines produced by injection molding (Howard et al., JDR, 59, 824-830, 1985), saucer-like molds, cylindrical molds, rectangle sheets, nylon mesh, and taper molds (Mueller et al., J. of Prosth. Den., 69, 367, Abstr. 2072, 1993). A wax mold of a simulated crown has also been designed (Bessing et al., Acta Odontology Scandinavian, 44, 165-172, 1986).

Titanium is inherently difficult to cast due to its high melting point and high reactivity. Its low density is another problem in casting. Therefore, the improvement of casting process is the main issue of titanium precision casting. The casting machines used at present utilize argon as the protective atmosphere to prevent high temperature reactions. Induction or arc is used as the heat source in order to shorten melting time as well as lessen high temperature reactivity. At present, in order to increase the pouring force and to avoid casting defect caused by poor flowability of the molten metal, the titanium casting machines can be roughly divided into the centrifugal casting type, the vacuum-pressure type, and the centrifugal-vacuum pressure mixed type (Yoshiaki, Conference Paper, 1-7, Australia, 1995).

U.S. Patent Number 6,572,815B1 discloses a technique to improve the castability of pure titanium by doping an alloying metal in an amount of 0.01 to 3 wt%, preferably 0.5 to 3 wt%, and more preferably about 1 wt%. Among various alloying metals used in this application bismuth is found the most promising element.

US patent No. 2,797,996 discloses titanium base alloys of high strength and ductility, and also of contamination resistance and high strength at elevated temperatures, which contain as essentially constituents titanium and tin, together with one or more additional metals selected from the groups comprising alpha promoters, beta promoters and compound formers. A large number of Ti-Sn base alloys were prepared in this patent, including ternary titanium alloys containing 1-5 wt% Bi. However, there is no teaching as to the improvement of castability or reducing surface tension of pure titanium or a titanium alloy.

US patent No. 4,810,465 discloses a free-cutting Ti alloy. The basic alloy composition of this free-cutting Ti alloy essentially consists of at least one of S: 0.001-10%, Se: 0.001-10% and Te: 0.001-10%; REM: 0.01-10%; and one or both of Ca: 0.001-10% and B: 0.005-5%; and the balance substantially Ti. The Ti alloy includes one or more of Ti-S (Se, Te) compounds, Ca-S (Se, Te) compounds, REM-S (Se, Te) compounds and their complex compounds as inclusions to improve machinability. Some optional elements can be added to above basic composition. Also disclosed are methods of producing the above free-cutting Ti alloy and a specific Ti alloy which is a particularly suitable material for connecting rods. Bismuth up to 10% was suggested in this free-cutting Ti alloy. However, there is no teaching as to the improvement of castability or reducing surface tension of pure titanium or a titanium alloy.

US patent No. 5,176,762 discloses an age hardenable beta titanium alloy having exceptional high temperature strength properties in combination with an essential lack of combustibility. In its basic form the alloy contains chromium, vanadium and titanium the nominal composition of the basic alloy being defined by three points on the ternary titanium-vanadium-chromium phase diagram: Ti-22V-13Cr, Ti-22V-36Cr, and Ti-40V-13% Cr. The alloys of the invention

are comprised of the beta phase under all the temperature conditions, have strengths much in excess of the prior art high strength alloys in combination with excellent creep properties, and are nonburning under conditions encountered in gas turbine engine compressor sections. Bismuth up to 1.5% was suggested in this age hardenable beta titanium alloy. However, there is no teaching as to the improvement of castability or reducing surface tension of pure titanium or a titanium alloy.

Summary of the Invention

A primary object of the present invention is to provide a medical device made of a titanium alloy having an improved castability.

Another object of the present invention is to provide a method of improving a castability of a titanium alloy.

A further object of the present invention is to provide a method of using a titanium alloy in making a medical device.

The present invention discloses a method for improving a castability of a titanium alloy comprising at least one alloy element selected from the group consisting of Mo, Nb, Ta, Zr and Hf, said method comprising introducing about 0.01-5 wt% Bi into said titanium alloy, preferably 0.1-3 wt% Bi, based on the weight of Bi and said titanium alloy.

Preferably, said titanium alloy further comprises at least one eutectoid beta stabilizing element selected from the group consisting of Fe, Cr, Mn, Co, Ni, Cu, Ag, Au, Pd, Si and Sn.

Preferably, the titanium alloy is substantially free from V.

Preferably, the titanium alloy is substantially free from Al.

Preferably, said titanium alloy consists essentially of Ti and Mo; Ti and Nb; Ti and Zr; Ti, Mo and Fe; Ti, Mo and Cr; Ti, Mo and Nb; Ti, Mo and Ta; Ti, Nb and Fe; Ti, Ta and Fe; Ti, Nb and Zr; Ti, Al and Nb; Ti, Mo, Zr and Fe; or Ti, Mo, Hf and Fe.

Brief Description of the Drawings

The present invention will be described in detail with reference to the illustrated embodiments and the accompany drawings, in which:

Fig. 1 is a schematic drawing showing the copper mold used for the castability test in the present invention;

Fig. 2 shows the effect on castability by doping 1 wt%, 3 wt% and 5 wt% of bismuth to commercially pure titanium (c.p. Ti) and a Ti alloy containing 7.5 wt% Mo and the balance Ti (Ti-7.5Mo) according to the present invention;

Fig. 3 shows the effect on castability by doping 1 wt%, 3 wt% and 5 wt% of bismuth to a Ti alloy containing 6 wt% Al, 4 wt% V and the balance Ti (Ti6Al4V) according to the present invention; and

Fig. 4 shows the effect on castability by doping 1 wt% of bismuth to various titanium alloys according to the present invention, wherein the numerals before the elements in the Ti alloys represent the weight percentage thereof.

Detailed Description of the Invention

The present invention provides a medical device made of a biocompatible titanium alloy composition having an improved castability comprising:

(a) about 0.01-5 wt% Bi, preferably 0.1-3 wt% Bi, based on the weight of the alloy composition;

(b) at least one alloy element selected from the group consisting of Mo, Nb, Ta, Zr and Hf; and

(c) the balance Ti.

The present invention also provides a method of using a titanium alloy composition in making a medical device comprising casting the above-mentioned biocompatible titanium alloy composition.

Preferably, said alloy composition further comprises at least one eutectoid beta stabilizing element selected from the group consisting of Fe, Cr, Mn, Co, Ni, Cu, Ag, Au, Pd, Si and Sn.

Preferably, said titanium alloy composition is substantially free from V.

Preferably, the titanium alloy composition is substantially free from Al.

Preferably, the titanium alloy composition consists essentially of Ti and Mo; Ti and Nb; Ti and Zr; Ti, Mo and Fe; Ti, Mo and Cr; Ti, Mo and Nb; Ti, Mo and Ta; Ti, Nb and Fe; Ti, Ta and Fe; Ti, Nb and Zr; Ti, Al and Nb; Ti, Mo, Zr and Fe; or Ti, Mo, Hf and Fe, in addition to Bi.

Preferably, the medical device is a dental casting.

Preferably, the medical device is a medical implant.

Example 1: c.p. Ti and Ti-Mo alloys doped with 1 wt%, 3 wt% and 5 wt% of Bi

In this example 0, 1, 3 and 5 wt% of bismuth of 99.5% in purity were melted into a grade II commercially pure titanium (c.p. Ti) and Ti-7.5Mo alloy containing 7.5 wt% of Mo and the balance Ti by using a commercial arc-melting vacuum/pressure type casting system (Castmatic, Iwatani Corp., Japan). Appropriate amounts of c.p. Ti, molybdenum and bismuth were melted in a U-shaped copper hearth with a tungsten electrode. The melting chamber was first evacuated and purged with argon. An argon pressure of 1.8 kgf/cm^2 was maintained during melting. After solidification/cooling in the same chamber in argon atmosphere, the thin oxidized layer of the ingot was removed by grinding and the ground surface was ultrasonically cleaned in alcohol. The ingot was re-melted three times to improve chemical homogeneity.

Prior to casting, the ingot was re-melted again in an open-based copper hearth under an argon pressure of 1.8 kgf/cm^2. The molten alloy instantly dropped from the open-based copper hearth into a copper mold located in a second chamber at room temperature via a pouring gate because of the pressure difference between the two chambers. As shown in Fig. 1, the pouring gate 20 has an inlet of 20 mm diameter and an outlet of 10 mm diameter, and a thickness of 18 mm between the inlet and the outlet. The copper mold 10 has two parallel needle-shaped cavities of 1 mm x 53 mm (diameter x length).

Cast lengths (a measure of castability) of undoped and Bi-doped c.p. Ti as well as Ti-7.5Mo alloy are compared in Fig. 2. As shown in the figure, when 1 or 3 wt% Bi was doped in c.p. Ti, the cast length increased by about 12%. When 5 wt% Bi was added, however, the castability value declined. This “up

and down" phenomenon was observed in a more dramatic way in Ti-7.5Mo system. When 1 wt% Bi was doped in Ti-7.5Mo alloy, the cast length largely increased by 34%. Again, when larger amounts of bismuth were added, the castability values decreased.

According to the theory of Ragone et al. [RAGONE, D. V. ADAMS, C. M., and TAYLOR, H. F. (1956) Some Factors Affecting Fluidity of Metals. AFS Trans., 64, 640.], addition of an alloy element to a pure metal always lowers the fluidity (increasing viscosity) of the metal due to the formation of dendrites that causes resistance to fluid flow at the early stage of solidification. This factor might satisfactorily explain why the castability value decreased when a relatively large amount (3 or 5 wt%) of bismuth was added. However, the dendrite factor could not explain the increase in castability when only 1 wt% Bi was added.

Example 2: Ti6Al4V alloy doped with 1 wt%, 3 wt% and 5 wt% of Bi

The procedures in Example 1 were repeated except that a commercially available Ti-6Al-4V alloy (Titanium Industries, Parsippany, NJ, USA) was used to replace c.p. Ti and Mo metals. The results are shown in Fig. 3.

From the measurement of casting lengths (a measure of castability, Fig. 3), it is interesting to note that the castability of Ti-6Al-4V alloy could be largely enhanced by almost 30% by the addition of 1 wt% Bi in the alloy, compared to that of undoped one. When a larger amount (3 or 5 wt%) of bismuth was added, however, the castability value of Ti-6Al-4V was not improved.

Example 3: castability of some commercial Ti alloys with 1 wt% Bi doped and without Bi doped

The procedures for preparing the doped and undoped Ti-7.5Mo alloys in Example 1 were repeated to prepare Ti7.5Mo-Fe alloys with 1 wt% Bi doped and without Bi doped except that an additional metal Fe was added in an amount of 1, 3 and 5 wt%, separately.

The procedures for preparing the doped and undoped Ti-7.5Mo alloys in Example 1 were repeated to prepare Ti15Mo alloy with 1 wt% Bi doped and without Bi doped except that the amount of Mo added was 15 wt%.

The procedures in Example 1 were repeated except that commercially available alloys TMZF (12 wt% of Mo, 6 wt% of Zr, 2 wt% of Fe, and the balance Ti) (Titanium Industries, Parsippany, NJ, USA), Ti13Nb13Zr (13 wt% of Nb, 13 wt% of Zr and the balance Ti) (Titanium Industries, Parsippany, NJ, USA), Ti5Al2.5Fe (5 wt% of Al, 2.5 wt% of Fe and the balance Ti) (Titanium Industries, Parsippany, NJ, USA), Ti6Al7Nb (6 wt% of Al, 7 wt% of Nb and the balance Ti) (Titanium Industries, Parsippany, NJ, USA), and Ti7Mo7Hf1Fe (7 wt% of Mo, 7 wt% of Hf, 1 wt% of Fe and the balance Ti) (Titanium Industries, Parsippany, NJ, USA) were used to replace c.p. Ti and Mo metals. The results are shown in Fig. 4 together with the 1 wt% Bi doped and undoped c.p. Ti, Ti7.5Mo, Ti6Al4V alloys prepared in Examples 1 and 2.

From the measurement of casting lengths (a measure of castability, Fig. 4), it can be seen that the castability of Ti alloys enhanced by the addition of 1 wt% Bi in the alloy ranges from about 17% (Ti5Al2.5Fe) to about 115% (Ti7.5Mo5Fe), compared to that of undoped one, while the castability improvement for c.p. Ti by the addition of 1 wt% Bi is only about 12%.

More examples of titanium alloys were prepared and the castability thereof was evaluated following the procedures recited in Example 1. The results are show in the following Table 1 together with those of the alloys prepared in Examples 1 and 3.

Table 1. Improvement in castability (cast length) of Ti alloys due to the presence of Bi

Ti alloy composition (wt%)	Cast length (mm)	Improvement in cast length (%)
Ti-7.5Mo	11.5	---
Ti-7.5Mo-1Bi	15.4	33.9
Ti-7.5Mo-3Bi	13.6	18.3
Ti-7.5Mo-5Bi	12.0	4.3
Ti-7.5Mo-1Fe	7.3	---
Ti-7.5Mo-1Fe-1Bi	13.1	79.5
Ti-7.5Mo-2Fe	8.3	---
Ti-7.5Mo-2Fe-0.1Bi	11.1	33.7
Ti-7.5Mo-2Fe-0.5Bi	12.7	53.0
Ti-7.5Mo-2Fe-1Bi	13.5	62.7
Ti-7.5Mo-3Fe	6.9	---
Ti-7.5Mo-3Fe-1Bi	12.6	82.6
Ti-7.5Mo-5Fe	6.8	---
Ti-7.5Mo-5Fe-1Bi	14.5	113.2
Ti-7.5Mo-2Cr	12.5	---
Ti-7.5Mo-2Cr-1Bi	13.7	9.6
Ti-15Mo	12.7	---
Ti-15Mo-1Bi	16.2	27.6
Ti-15Mo-3Bi	14.8	16.5
Ti-15Mo-5Nb	12.9	---
Ti-15Mo-5Nb-1Bi	15.4	19.4
Ti-15Mo-5Ta	12.0	---
Ti-15Mo-5Ta-1Bi	13.0	8.3
Ti-15Mo-2Fe	8.2	---
Ti-15Mo-2Fe-1Bi	9.8	19.5
Ti-15Mo-2Cr	12.3	---
Ti-15Mo-2Cr-1Bi	16.7	35.8
Ti-20Mo	12.6	---
Ti-20Mo-1Bi	15.7	24.6

Table 1 (continued)

Ti alloy composition (wt%)	Cast length (mm)	Improvement in cast length (%)
Ti-10Nb	10.8	---
Ti-10Nb-1Bi	18.5	71.3
Ti-25Nb	10.5	---
Ti-25Nb-1Bi	14.7	40.0
Ti-25Nb-2Fe	7.0	---
Ti-25Nb-2Fe-1Bi	9.2	31.4
Ti-25Ta-2Fe	7.2	---
Ti-25Ta-2Fe-1Bi	8.4	16.7
Ti-35Nb	8.0	---
Ti-35Nb-1Bi	11.2	40.0
Ti-12Mo-6Zr-2Fe	9.2	---
Ti-12Mo-6Zr-2Fe-1Bi	11.1	20.7
Ti-13Nb-13Zr	9.2	---
Ti-13Nb-13Zr-1Bi	14.5	57.6
Ti-5Al-2.5Fe	10.8	---
Ti-5Al-2.5Fe-1Bi	12.6	16.7
Ti-6Al-7Nb	14.1	---
Ti-6Al-7Nb-1Bi	17.2	22.0
Ti-7Mo-7Hf-1Fe	8.0	---
Ti-7Mo-7Hf-1Fe-1Bi	10.5	31.2
Ti-30Zr	13.2	---
Ti-30Zr-1Bi	14.1	6.7